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OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 400x056yip01&02

Technical Report No. 12

Thermoset Precursor to Monolithic Carbon Glass Prepared by the Pd/Cu-Catalyzed Alkynylation of Polyphenylenes.

by

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Accepted for Publication in

Polymer Preprints (Am. Chem. Soc., Div. Polym. Chem.)

April 25, 1992

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
April 25, 1992

3. REPORT TYPE AND DATES COVERED
Technical Report # 12

4. TITLE AND SUBTITLE
Thermoset Precursor to Monolithic Carbon Glass Prepared by the Pd/Cu-Catalyzed Alkynylation of Polyphenylenes

5. FUNDING NUMBERS
G- N00014-89-J3062
R&T 400x056yip01601

6. AUTHOR(S)
Eric B. Stephens and James M. Tour

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

8. PERFORMING ORGANIZATION REPORT NUMBER
N00014-89-J3062

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Polymer Preprints (Am. Chem. Soc., Div. Polym. Chem.)

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The functionalization of (bromophenyl)oligophenylene with several alkynes is described. The bromide groups on the oligomer were replaced with terminal alkynes using a Pd/Cu catalysts system. Substitution of nearly all the original bromide locations was achieved. The functionalized oligomers, freely soluble in THF, exhibited high char yields on thermolysis to 900°C under a nitrogen atmosphere. Several of the functionalized oligomers flowed on heating. The oligomer that was functionalized with phenylacetylene exhibited a well-defined melting point at 190°C and acetylenic coupling did not take place until 310°C. The hot oligomer flowed to form a monolith of glassy carbon. Depending on the alkyne used, a range of densities from 1.39-1.95 g/cc could be obtained in the final carbon glass. The structure/property relationships and the material applications are discused.

14. SUBJECT TERMS
Thermosets, glassy carbon, high density, polyphenylene, cross coupling

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Thermoset Precursor to Monolithic Carbon Glass Prepared by the Pd/Cu-Catalyzed Alkynylation of Polyphenylenes

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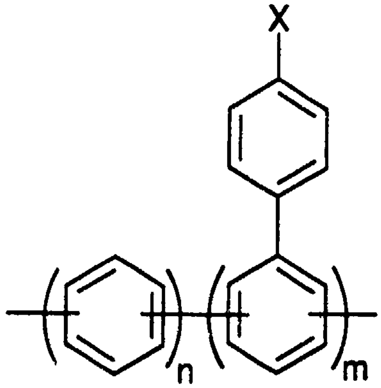
Carbon materials produced by the thermolysis of organic polymers have been used for numerous applications in, for example, the aerospace, electronic, and automotive industries.[2] Development of high char yielding carbon materials from alkyne-containing organics has been investigated by many; unfortunately, the difficulty in preparing the alkyne-containing monomers and the explosive nature of the multi-alkynylaromatics has retarded the rapid development and commercialization of this process.[3]

We describe here the synthesis of a polymer possessing two required features that make it suitable for a thermoset precursor to glassy carbon. First, the polymer has very low weight loss (high char yield) on conversion to glassy carbon so that significant void volume will not result in the molds. Second, the material exhibits a well-defined melting point, even a gravity-induced flowing, prior to conversion to carbon so that processing in the melt is possible to produce carbon monoliths. Though many carbon applications do not require these two features, they are a necessity if the material is to have uses as a thermoset precursor. Such precursors may have wide-spread applications ranging from uses in electronic components to rocket booster ablatives.[2,3]

We previously described a one step synthesis of brominated polyphenylenes from 1,4-dibromobenzene in dioxane with HMPA.[4,5] Recently, we described an alternative procedure that does not require the use of the cancer suspect agent HMPA and affords a 65% yield of an ether insoluble portion of **1a** ($n = m$) but possessing less para linkages than the polymer prepared by the HMPA method (Figure I).[6] All polymers prepared were soluble in THF. Though **1a** exhibits a high carbon to hydrogen (C/H) ratio, neither the brominated polymer **1a** nor the debrominated material **1b**[7] exhibited high char yields on heating (Table I).

In order to enhance the char yield, we needed to prevent volatilization on heating by appending a suitable thermo-activated cross-linking substituent.

Figure I



1a, X = Br

1b, X = H

1c, X = $\equiv$—H

1d, X = $\equiv$—$SiMe_3$

1e, X = $\equiv$—C_6H_{13}-n

1f, X = $\equiv$—Ph

1g, X = $\equiv$—(p-C_6H_4)-Ph

1h, X = $\equiv$—(p-C_6H_4)—$\equiv$—Ph

1i, X = $\equiv$—(m-C_6H_4)—$\equiv$—Ph

1j, X = $\equiv$—(1-Naph)

Table I

#	M_w[c]	M_w/M_n	% Wt Loss[d]	T_g[e,f]	T_m[f,g]	T_{exo}[f,h]
1a[a]	1944	3.89	48	---	155, 170	NA
1b	2323	2.68	52	---	170, 225	NA
1c[b]	3834	3.92	17.5	182	---	360
1d	3758	6.63	27	---	140	160
1e	3327	3.32	33	---	140	170
1f	2709	2.80	13.5	---	190	310
1g	3610	3.02	15.5	---	205	310
1h	4089	3.53	11.5	206	---	350
1i	3734	3.21	10.7	203	---	350
1j	3588	2.07	12.9	---	200	230

[a]Prepared in THF without HMPA according to ref 6. All other compounds in this Table were prepared from **1a** except **1e** which was prepared from the brominated polymer made with HMPA as in ref 4. [b]Prepared by treatment of **1d** with K_2CO_3 in THF/CH_3OH. [c]Determined by size exclusion chromatography relative to polystyrene. [d]Total percent weight loss by thermogravimetric analysis (TGA) from ambient to 900°C at 20°C/min under an N_2 atmosphere. [e]Polymer glass transition temperature. [f]Determined by differential scanning calorimetry (DSC) from 60°- 500°C at 20°C/min under an N_2 atmosphere. Dashed lines signify that the these values were not clearly discernable by the DSC. [g]Polymer melt temperature. [h]Large exotherm characteristic of alkyne couplings. NA means not applicable.

However, the moiety must not cross-link prior to the polymer melting or else the desired flow properties would not be maintained. Moreover, the introduction of heteroatoms would be prohibited if a high char yield of carbon materials was to be achieved. Hence, we investigated the metal-catalyzed functionalization of **1a** that would concomitantly replace the bromide heteroatoms. Following the Stephans-Castro/Sonogashira protocol,[8] **1a** was treated with various terminal alkynes in a THF solution containing diisopropylamine, both a CuI catalysts and $Cl_2Pd(PPh_3)_2$ or $Pd(PPh_3)_4$ catalyst (23°C for 1 h, 60°C for 10 h, and 100°C for 5 h in a threaded screw cap reaction tube) to produce **1d-j**. In most cases, complete bromide substitution was achieved as determined by elemental analysis.[9]

Several structure/property relationships were clearly evident and allowed us to rapidly converge on a thermoset precursors for glassy carbon. Though **1c** exhibited a high char yield, the terminal alkyne was too unhindered and the cross-linking event occurred without a well-defined melt by DSC analysis. Polymers **1d** and **1e** had more hindered alkynes than **1c** and they exhibited well-defined melts; however, the introduction of the aliphatic material decreased the C/H ratio resulting in a lower char yield than desired. Remarkably, by simply substituting **1a** with phenyl acetylene to produce **1f** (amorphous by powder x-ray diffraction (XRD)), we obtained a very high char yield and the polymer exhibited a well-defined melt at 190°C while the coupling event did not occur until 310°C by DSC analysis. *Hence a 120°C processing window exists for this glassy carbon precursor.* Gravity flow of the melted material occurred to form a glossy black, void free monolithic disc of glassy carbon. Powder XRD of the charred material from the thermolysis of **1f** confirmed the presence of glassy carbon with no signals for the graphitic crystallite. The polydispersity of **1f** could be lowered by purification of the polymers by fractional precipitation, however, the flow properties then decreased significantly. Likewise, when we phenylacetylated a brominated polyphenylene having more para linkages prepared by the HMPA route,[4] the flow properties on thermolysis were also impaired. Thus more rigid polymer backbones are inferior. Compounds **1g-j** were also prepared and studied; however, they offered no advantage over **1f**. Though the char yields were slightly better for **1h-j**, the final carbon glass had not flowed as significantly as in the case of **1f**.[10] Moreover, the reagent necessary for **1f**, phenylacetylene, is commercially available.

Hence, organometallic methods permitted a two step (polymerization and functionalization) entry into a thermoset precursors for glassy carbon that does not require the multi-step step preparation of highly reactive and often explosive di- or trialkynylaromatics.

General procedure for coupling terminal acetylenes to 1a. The procedure by Sonogashira[8a] was modified as follows. To a screw cap tube containing **1a** (0.29 g, estimated 0.96 mmol of Br), copper(I) iodide (0.04 mmol, 4.0 mol%), dichlorobis(triphenylphosphine)palladium(II) or tetrakis(triphenylphosphine)palladium(0) (0.05 mmol, 4.5 mol%) in THF (3 mL) was added at room temperature a terminal acetylene (2.9 mmol, 3.5 eq) and diisopropylamine (2.9 mmol, 3.5 eq). The black reaction solution was stirred at room temperature for 1 h then warmed to 60°C for 10 h and 100°C for 5 h. The reaction mixture was allowed to cool to room temperature and poured into water (20 mL). The organic layer was separated and the aqueous portion extracted with methylene chloride (3x). The combined organic layers were washed with aqueous ammonium chloride (3x). Filtration and removal of the solvent *in vacuo* gave a brown oil which was usually stirred with ether and the ether insoluble solid was removed by filtration.

Acknowledgements. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Program (N00014-89-J-3062), the National Science Foundation (RII-8922165, DMR-9158315, DMR-9101539), and generous industrial donors to the NSF/PYI award: Hercules Incorporated, and the IBM Corporation. We thank Dr. T. Keller of the Naval Research Laboratories and Dr. H. Jabloner of Hercules Incorporated for helpful suggestions.

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(9) Less than 0.5% Br was detected by elemental analysis in **1e-j**. Compounds **1c** and **1e** showed 3.00% and 5.85% Br, respectively.

(10) The thermolyzed compounds had the following appearances after the TGA analyses: **1a** was a glossy black porous disc; **1b**, **1d**, **1e**, and **1g** each formed several glossy black droplets; **1c** was a black powder; **1h** and **1i** each formed dull gray meshes; **1j** formed a single glossy black droplet; and **1f** formed a glossy black void-free disc. Thus, in addition to **1f**, compounds **1g**, and **1j** appear to be suitable for glassy carbon thermosets if a pressure system is employed.